AD-A250 235

ATION PAGE

Form Approved
OMB No 0704-0188

DATE	3 REPORT TYPE AND DATES COVERED
4 5 92	Technical Report

4. TITLE AND SUBTITLE
Vibrational Spectrum and Structure of 1,2-Dimethyl-1,2-disila-closo-dodecaborane

5. FUNDING NUMBERS
N-00014-91-J1590

6. AUTHOR(S)
S.S. Bukalov, L.A. Leites, Lars Wesemann, Dietmar Seyferth

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Massachusetts Institute of Technology
Department of Chemistry
77 Massachusetts Avenue
Cambridge, MA 02139

8. PERFORMING ORGANIZATION REPORT NUMBER
36

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
4132038

11. SUPPLEMENTARY NOTES
to be incorporated into a full paper to be submitted to JACS

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The IR spectrum (thin film) of 1,2-dimethyl-1,2-disila-closo-dodecacarboran DMSB, in the region 200 - 3600 cm^{-1} and its Raman spectrum (solid sample) in t region 5 - 3600 cm^{-1} are reported. It is concluded that the molecular bonding in DMSB is weaker than that in o-carborane. A Raman band at 399 cm^{-1} is tentatively assigned to the Si-Si bond.

14. SUBJECT TERMS
boron compounds, organosilicon compounds, carborane analogs, IR and Raman spectroscopy

15. NUMBER OF PAGES
10

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABS
unclassified	unclassified	unclassified	unlimited

OFFICE OF NAVAL RESEARCH
CONTRACT N00014-91-J-1590
R & T Project Code 4132053

TECHNICAL REPORT NO. 36

VIBRATIONAL SPECTRUM AND STRUCTURE OF 1,2-DIMETHYL-1,2-DISILA-*CLOSO*-DODECABORANE

by

S.S. Bukalov, L.A. Leites, Lars Wesemann, Dietmar Seyferth

To Be Incorporated Into
A Full Paper
To Be Submitted To *JACS*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

April 5, 1992

Vibrational Spectrum and Structure of 1,2-Dimethyl-1,2-disila-*closo*-dodecaborane

S.S. Bukalov, L.A. Leites
Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilova 28, Moscow 117813, Russia

Lars Wesemann and Dietmar Seyferth
Department of Chemistry, Massachusetts Institute of Technology, Cambridge MA 02139, USA

ABSTRACT

The IR spectrum (thin film) of 1,2-dimethyl-1,2-disila-*closo*-dodecacarborane DMSB, in the region 200-3600 cm^{-1} and its Raman spectrum (solid sample) in the region 5 - 3600 cm^{-1} are reported. It is concluded that the molecular bonding in DMSB is weaker than that in *o*-carborane. A Raman band at 399 cm^{-1} is tentatively assigned to the Si–Si bond.

Recently, 1,2-dimethyl-1,2-disila-*closo*-dodecaborane (or briefly dimethyl-*o*-silaborane), shown in Fig. 1, the first silicon analog of *o*-carborane, was synthesized and studied by X-ray and NMR methods.[1] We report and discuss here the vibrational spectrum of this compound. Its Raman spectrum in the region 5 - 3600 cm^{-1} was obtained for the solid sample at different temperatures; polarization measurements of Raman lines were carried out for its saturated solution in benzene. The IR spectrum of a thin film sublimed onto a cold target of the cryostat was measured in the region 200 - 3600 cm^{-1}. The results obtained are presented in Fig. 2 and Table 1.

It is of interest to compare the spectrum of dimethyl-*o*-silaborane (DMSB) with those of other icosahedral species: the dodecaborate anion, $B_{12}H_{12}^{2-}$,[2] and *o*-carborane, $C_2B_{10}H_{12}$.[3,4]

The DMSB molecule belongs to the C_{2v} symmetry point group. The 66 normal vibrations of the $B_{10}H_{10}(SiC)_2$ moiety are distributed among the symmetry species as follows:

$$\Gamma = 21\ A_1 + 13\ A_2 + 16\ B_1 + 16\ B_2.$$

All these species should be active in the Raman and all but A_2 in the IR.

In fact, as is seen from Fig. 2, almost all Raman lines have their IR counterparts. This is in contrast to *o*-carborane, which belongs formally to the same point group C_{2v} and has the same selection rules, but whose spectrum really obeys the higher effective symmetry of an averaged icosahedron.

The most prominent features of the vibrational spectra of all *closo*-boranes are the ν(BH) multiplet in the region 2400 - 2600 cm^{-1} and the polyhedron "breathing" mode near 750 cm^{-1}. In the case of DMSB the ν(BH) multiplet is centered near 2550 cm^{-1} and the "breathing" mode at 715 cm^{-1}, both features being markedly shifted to lower frequencies compared to *o*-carborane. These modes being well localized, this shift indicates a weakening of molecular bonding in DMSB as compared to that in *o*-carborane. However, the ν(BH) band of DMSB is shifted to higher frequencies if compared to the average ν(BH) frequency 2480 cm^{-1} of the $B_{12}H_{12}^{2-}$ anion.

The most striking difference between the spectrum of DMSB and those of $B_{12}H_{12}^{2-}$ and *o*-$C_2B_{10}H_{12}$ is the presence in the former of low-frequency modes, equally intense in the Raman and IR spectra. The most intense in the Raman spectrum is the strongly polarized narrow line at 399 cm^{-1}. Its frequency coincides with that of the ν(Si–Si) mode of hexamethyldisilane.[5] Thus it seems reasonable to assign this line to the Si–Si stretching mode. However, this assigment is tentative and needs to be proved by a normal

coordinate analysis, because a heavily mixed origin of this mode cannot be excluded.

It is evident that all the rest of the low-frequency bands of DMSB are associated with participation of the silicon atoms in the cage motions, because the spectra of the rigid $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ polyhedra exhibit no bands with frequencies lower than 450 cm^{-1}.

The polarized Raman line at 640 cm^{-1} seems to correspond to the symmetrical stretch of the exo-polyhedral Si–C bonds; its frequency lies in the usual range and is close to that of the Si–C bonds in $(CH_3)_3SiCl$.[6] The frequencies of the internal vibrations of the methyl groups attached to the silicon atoms, i.e., 1260, 1395, 2913 and 2993 cm^{-1}, also are much the same as those in the spectra of the methylchlorosilanes, in particular, CH_3SiCl_3,[6] which is in accord with the well-known electron-deficient nature of the *closo*-borane cage.

The DMSB molecule obviously is "globular", in the sense of Timmermans.[7] However, unlike icosahedral carboranes,[4,8] this substance does not form a plastic phase at room temperature, which is evident from the presence of the lattice modes in the low-frequency region of its Raman spectrum (Fig. 2).[9] Heating of the substance to 70°C revealed no phase interruption to a plastic phase in this temperature interval.

EXPERIMENTAL

DMSB was synthesized according to ref. 1. The sample was thoroughly purified by several successive sublimations *in vacuo* just before the spectra were taken. *The substance is not as stable to atmosphere moisture and oxygen as stated in ref. 1.* After the thin film of DMSB obtained by sublimation *in vacuo* on a cold target of the cryostat was exposed to the atmosphere, its IR spectrum soon acquired some "extra" bands, namely ~3200

cm^{-1} [ν(B–OH)], ~1200 cm^{-1} [δ(B–OH)] and ~1100 cm^{-1} [ν(SiOSi)], which indicated partial oxidation of the material. The intensity of the "extra" bands slowly increased with time (see Fig. 3).

Raman spectra were obtained using a Ramanov HG-2S spectrometer equipped with an ILA-2 argon ion laser, operating at 5145 Å as the exciting source. The exciting power was less than 100 mW. IR spectra were measured with a M-80 Karl Zeiss spectrophotometer and a Bruker IFS-113v Fourier transform spectrometer.

Acknowledgement. The research at MIT was supported in part by the Office of Naval Research.

REFERENCES

1. D. Seyferth, K. Büchner, W.S. Rees Jr., W.M. Davis *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 918.
2. L.A. Leites, S.S. Bukalov, A.P. Kurbakova, M.M. Kagansky, Yu.L. Gaft, N.T. Kuznetsov, I.A. Zakharova *Spectrochim. Acta*, **1982**, *38A*, 1047.
3. L.A. Leites, L.E. Vinogradova, V.T. Alexanyan, S.S. Bukalov *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 2480 (Proceedings of the Soviet Academy of Sciences, Chemical Ser.).
4. S.S. Bukalov, L.A. Leites *Chem. Phys. Lett.*, **1982**, *87*, 327.
5. B. Fontal, T.G. Spiro *Inorg. Chem.*, **1971**, *10*, 9.
6. V.S. Dernova, I.F. Kovalev "Kolebatelnye Spektry Soedinenii Elementov IVB Gruppy" (Vibrational Spectra of Compounds of IVB Group Elements), Saratov University Press 1979, p. 154.
7. J. Timmermans *J. Chem. Phys.*, **1938**, *36*, 331.
8. L.A. Leites, S.S. Bukalov *J. Raman Spectroscopy*, **1978**, *7*, 235; **1983**, *14*, 210.
9. S.S. Bukalov, L.A. Leites *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **1989**, *53*, 1715 (Proc. of the Soviet Academy of Sciences, Phys. Ser.).

CAPTIONS

Fig. 1 1,2-dimethyl-1,2-disila-*closo*-dodecaborane(12).

Fig. 2 Vibrational spectrum of solid DMSB.

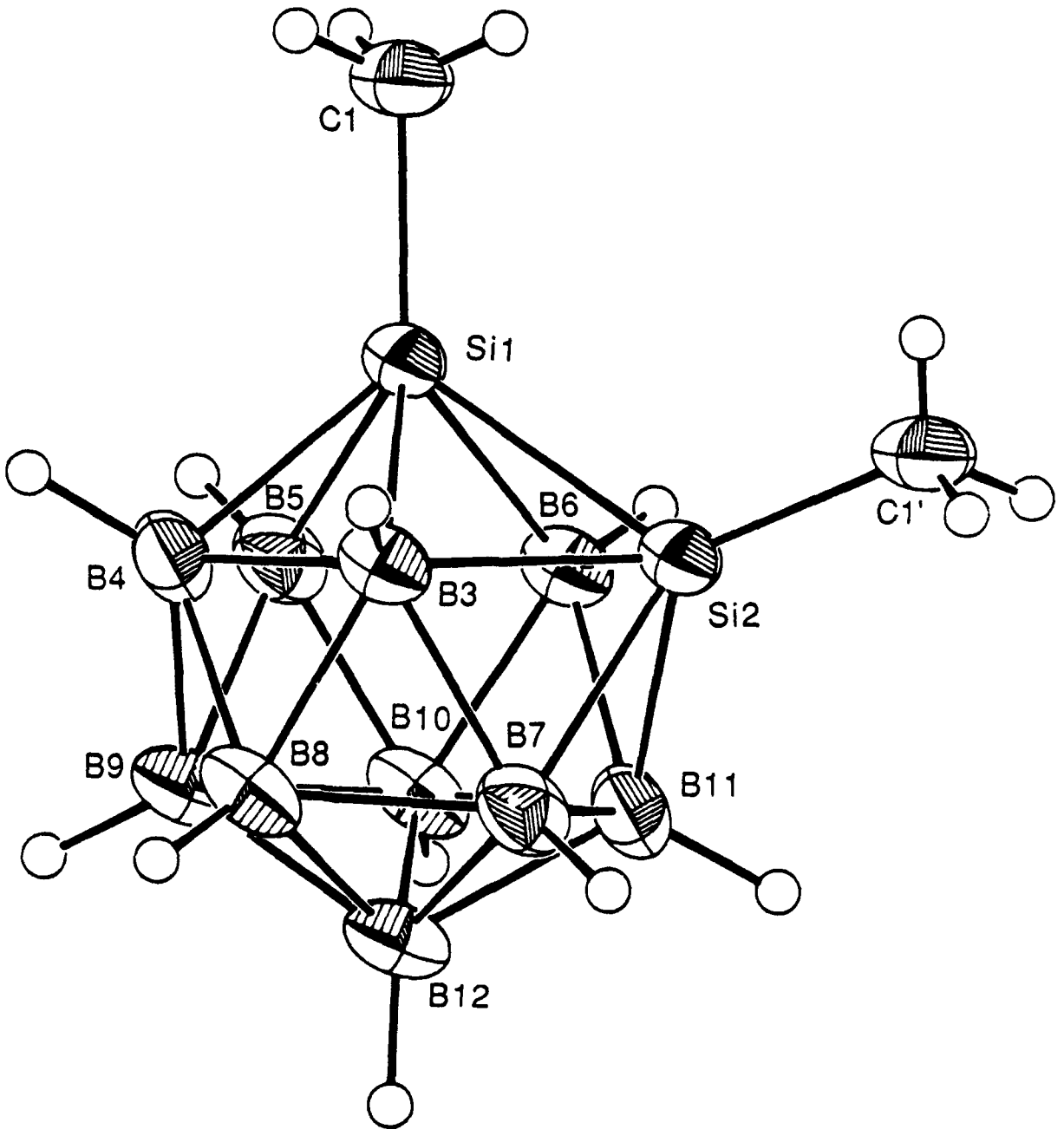
Fig. 3 Process of oxidation of DMSB in air as shown by its IR spectrum.

1. IR spectrum of a DMSB thin film just after sublimation *in vacuo* (no ν_{B-OH} bond at ~3200 cm^{-1}).
2. IR spectrum of the same sample after 5 hours of exposire to air.
3. The same on the next day.
4. The same after a week.

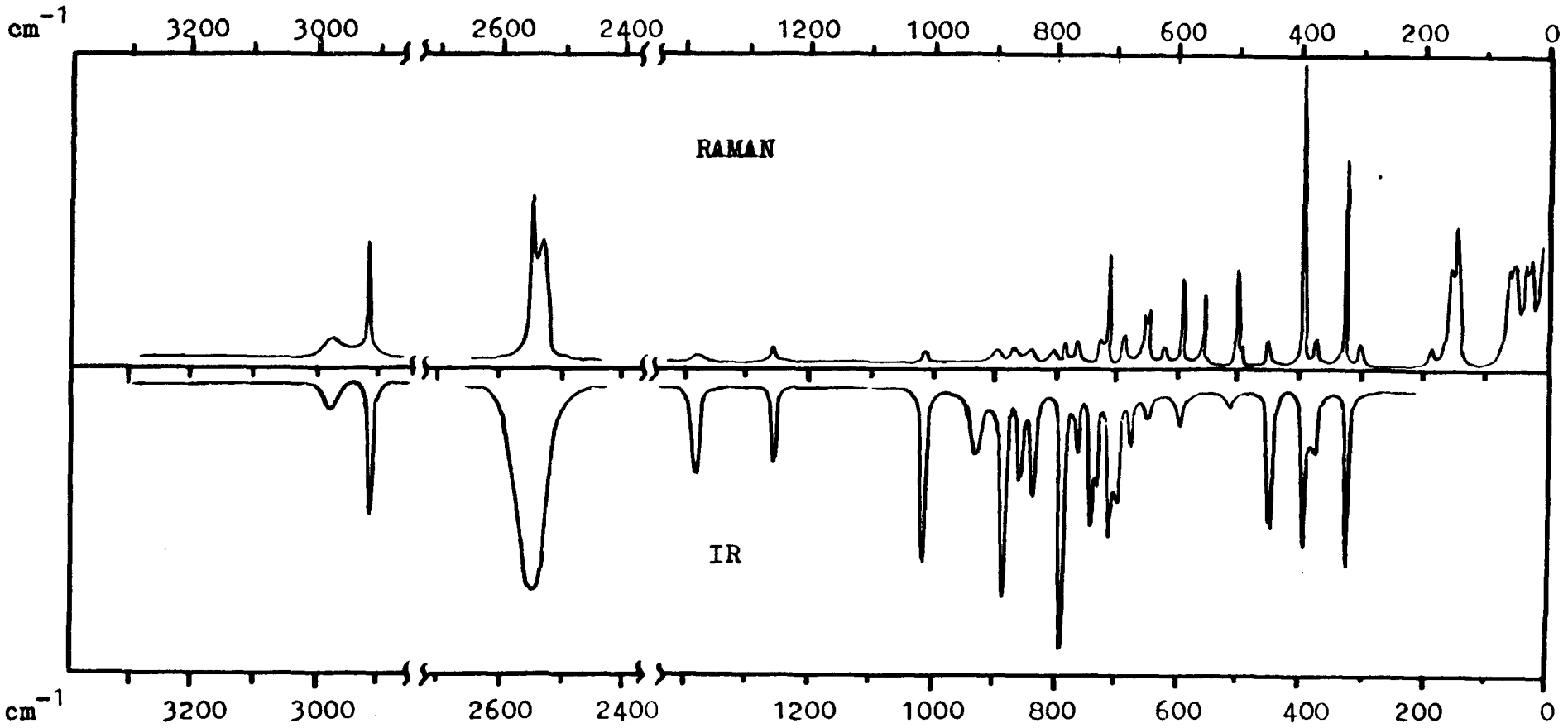
Table. Vibrational spectrum of $B_{10}H_{10}(SiMe)_2$

Raman			IR
Solid sample.	Solution in benzene		Vacuum sublimation on a cold target
$\Delta\nu$, cm^{-1}	$\Delta\nu$, cm^{-1}	ρ	ν, cm^{-1}
152 m.			
186 sh.			
306 w.			304 w.
329 s.	326	0.80	328 s.
379 w.			379 sh.
400 vs.	399	0.28	397 s.
449 w.			448 s.
503 m.	504	0.12	503 w.
550 m.	552	0.62	
587 m.			578 w.
610 w.			610 vw.
		p.	
645 m.			659 w.
686 w.			689 w.
716 s.	713	0.03	718 m.
758 w.			752 sh.
			759 m.
773 w.			775 w.
792 w.			793 vs.

841 w			848 m.
860 w.			862 w.
895 w.			886 s.
920 w.			916
			957 w.
1010 w.			1010 vs.
1260 w.			1246 w.
1392 w.			1395 m.
2547 s.	2549	0.16	2548 vs.
2556 vs.			
2913 m.			2908 s.
2994 wbr.			2991 wbr.



Fi


cm-1
3200
3000
2600
2400
1200
1000
800
600
400
200
0
RAMAN
IR
cm-1
3200
3000
2600
2400
1200
1000
800
600
400
200
0

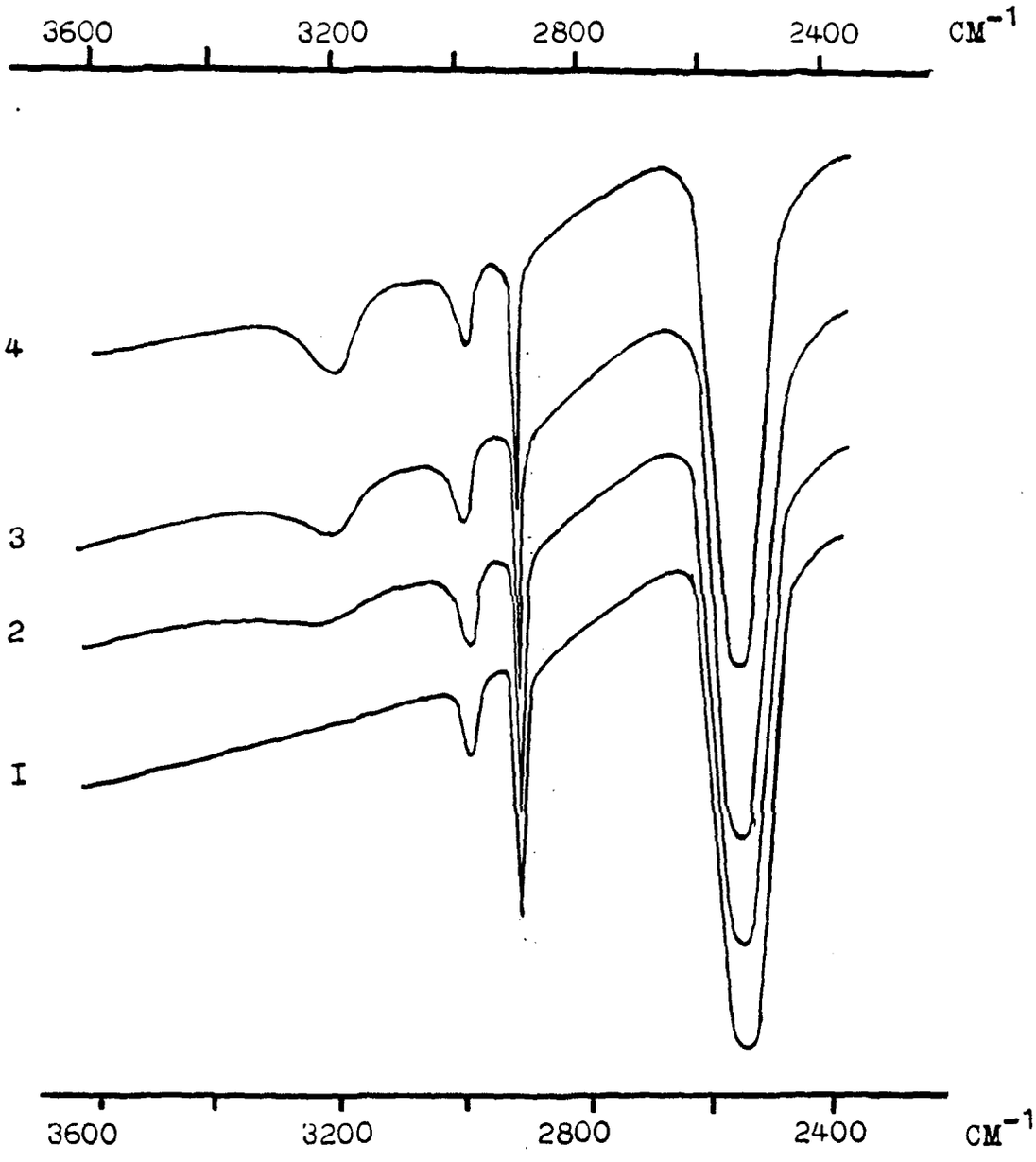


Fig. 3